

# Helium in solubility equilibrium with quartz and porefluids in rocks: A new approach in hydrology

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[1] Quartz crystals in sandstones at depths of 1200 m–1400 m below the surface appear to reach a solubility equilibrium with the  $^4\text{He}$ -concentration in the surrounding pore- or groundwater after some time. A rather high  $^4\text{He}$ -concentration of  $4.5 \cdot 10^{-3}$  cc STP  $^4\text{He}/\text{cm}^3$  of water measured in a groundwater sample would for instance maintain a He pressure of 0.47 atm in a related volume. This value is equal within analytical error to the pressure deduced from the measured helium content of the quartz and its internal helium-accessible volume. To determine this volume, quartz crystals of 0.1 to 1 mm were separated from sandstones and exposed to a helium gas pressure of 32 atm at a temperature of 290°C for up to 2 months. By crushing, melting or isothermal heating the helium was then extracted from the helium saturated samples. A volume on the order of 0.1% of the crystal volume is only accessible to helium atoms but not to argon atoms or water molecules. By monitoring the diffusive loss of He from the crystals at 350°C an effective diffusion constant on the order of  $10^{-9}$  cm<sup>2</sup>/s is estimated. Extrapolation to the temperature of 70°C in the sediments at a depth of 1400 m gives a typical time of about 100 000 years to reach equilibrium between helium in porewaters and the internal He-accessible volume of quartz crystals. In a geologic situation with stagnant pore- or groundwaters in sediments it therefore appears to be possible with this new method to deduce a  $^4\text{He}$  depth profile for porewaters in impermeable rocks based on their mineral record. *INDEX*

*TERMS:* 1832 Hydrology: Groundwater transport; 1894 Hydrology: Instruments and techniques; 1035 Geochemistry: Geochronology.

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## 1. Introduction

[2] All rocks contain uranium and thorium and therefore continuously produce  $^4\text{He}$  atoms by neutralization of  $\alpha$ -particles emitted in the natural series of radioactive decay. Generally, radiogenic helium is readily released from rocks, so that less than 10% of He produced since the rock was formed is retained [e.g., *Mamyrin and Tolstikhin*, 1984]. The released atoms reside in related groundwaters (or pore fluids) from where they are transported either by diffusion or water flow and are eventually discharged to the atmosphere. A comparison of calculated  $^4\text{He}$ -production rates (based on U- and Th-concentrations) and measured  $^4\text{He}$ -concentrations in rocks, minerals, porewaters and groundwaters in principle can help to understand the transport processes in subsurface water/rock environments. A primary goal in many applications related to waste repositories is the need to identify situations with long-term stagnant water. Furthermore, any attempt to estimate the capacity of aquifers (e.g., for drinking water supply) depends on a quantitative understanding of the situation underground.

[3] By analysing  $^4\text{He}$ -concentrations in porewaters extracted from freshly drilled rock cores it has recently become possible to establish depth profiles in impermeable rocks and understand diffusive  $^4\text{He}$ -transport in sedimentary basins on time scales of up to 10 million years [*Osenbrück et al.*, 1998; *Rübel et al.*, 2002]. Such an approach, however, is not only limited to situations where appropriate rock samples can be sealed into vacuum containers within roughly 30 minutes after core recovery from a deep borehole, but it also ignores the problems related to changes of the rock structure by both the drilling process as well as the sharp pressure decrease during core uplifting.

[4] In this contribution we investigate the possibility that minerals retain a memory of the pore fluid environment they were located in for long time intervals. Quartz grains separated from sandstone of the Permo-Carboniferous Trough in Northern Switzerland contain “excess helium”, i.e., more helium than could have been produced in-situ based on the measured U- and Th-concentrations during the

**Table 1.** Measured Noble Gas Abundances and Ratios and Calculated He-Accessible Volumes  $V_2$ 

Sample	Extraction	Fraction 1 initial noble gas abundances			Fraction 2 exposed for 504 hours		Fraction 3 exposed for 1412 hours	
		$^4\text{He}$ ( $\times 10^{-3}$ ) cc STP/cm <sup>3</sup>	$^3\text{He}/^4\text{He}$ ratio ( $\times 10^{-8}$ )	$^4\text{He}/^{40}\text{Ar}^*$ ratio	$^4\text{He}$ ( $\times 10^{-3}$ ) cc STP/cm <sup>3</sup>	$V_2$ (equation 1) $10^{-3}$ cm <sup>3</sup> /cm <sup>3</sup>	$^4\text{He}$ ( $\times 10^{-3}$ ) cc STP/cm <sup>3</sup>	$V_2$ (equation 1) $10^{-3}$ cm <sup>3</sup> /cm <sup>3</sup>
1150.71 m	crushing	0.11	10.1	62	5.5	<b>0.35</b>	4.9	<b>0.32</b>
	melting of crushed sample	0.094	6.7	29	2.8	<b>0.18</b>	3.1	<b>0.20</b>
1250.34 m	isothermal heating	0.32	10	71	16.0	<b>1.0</b>	20	<b>1.3</b>
1409.83 m	crushing	0.24	9.1	330	9.3	<b>0.60</b>	3.4	<b>0.22</b>
	melting of crushed sample	0.11	8.3	37	3.8	<b>0.25</b>	3.9	<b>0.25</b>

time since the sediments were formed [Tolstikhin *et al.*, 1996]. Furthermore, the measured  $^3\text{He}/^4\text{He}$ -ratio of  $8 \times 10^{-8}$  clearly points to a helium source in the adjacent Li-rich shales (calculated ratios for sandstone  $1.4 \times 10^{-8}$ , for shale  $7.2 \times 10^{-8}$ ). In this study we measure the internal free volumes accessible for helium of selected quartz crystals, their  $^4\text{He}$ -contents and compare them with the  $^4\text{He}$ -concentrations in groundwater samples collected from the same depth. It is proposed to use such data to determine the abundance of helium in pore fluids of impermeable rocks, an important parameter which cannot easily be obtained otherwise.

## 2. Samples

[5] The lithology and hydrogeology of the Molasse basin and the deep trough of permo-carboniferous sediments in Northern Switzerland as a whole is discussed by Pearson *et al.* [1991]. In this contribution we study quartz separates (generally with  $\sim 10\%$  contribution of feldspars) from arkosic sandstones encountered in the Weiach borehole (25 km north-west of Zürich) at the depth interval between 1150.71 m and 1409.83 m. The rocks are mainly composed of quartz ( $\sim 50\%$ , the grain size varies from 0.1 to 1 mm), K-feldspar ( $\sim 20\%$ ), plagioclase ( $\sim 10\%$ ), and matrix mineral cement ( $\sim 20\%$ ). The latter includes very fine grained quartz, sericite, chlorite, biotite and clay minerals.

## 3. Experimental

[6] From each of three selected sandstones, quartz minerals were separated and split into three equal fractions. The first fraction was used to determine the initial content of noble gases and isotope ratios. The two other fractions were used for He-impregnation, one for a shorter and one for a longer time interval (see below), in a specially designed cylindrical vessel which can withstand pressures of up to 150 atmospheres of He and temperatures up to 600°C.

[7] Three different devices were used for helium extraction from the samples: (i) crushing, (ii) heating under constant temperature and (iii) step-wise heating and/or fusion [Kamensky *et al.*, 1984; Ikorsky and Kusth, 1992]. In all cases the extracted gases were admitted to an all-metal line and purified using Ti-Zr getters. The abundances of He and Ar isotopes were measured using a static mass spectrometer (MI 1201) with a resolving power of  $\sim 1000$ , which allows a complete separation of  $^3\text{He}^+$  from  $^3\text{H}^+$  and  $\text{HD}^+$ . The sensitivity for He was  $5 \times 10^{-5}$  A torr<sup>-1</sup>, the lowest measurable  $^3\text{He}/^4\text{He}$  ratios being below  $10^{-8}$ . A mixture of pure  $^3\text{He}$ , helium from a high-pressure tank ( $^3\text{He}/^4\text{He} = 2 \times 10^{-8}$ ) and atmospheric He, Ne, Ar, Kr and

Xe was used as a standard for the calibration of the mass-spectrometer. The ratios of  $^3\text{He}/^4\text{He} = 1.6 \times 10^{-6}$  and  $^4\text{He}/^{20}\text{Ne} = 47$  in the mixture were measured using air as the primary standard in the Apatity laboratory. The concentrations of  $^4\text{He}$  and  $^{40}\text{Ar}$  were determined by the peak height method with an uncertainty of  $\pm 5\%$  ( $1\sigma$ ). Uncertainties in the  $^3\text{He}/^4\text{He}$  ratios of  $\sim 10^{-6}$  and  $\sim 10^{-8}$  were 2% and 20%, respectively, and uncertainties in the  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios of 300 and 50,000 were 0.3% and 25%, respectively. The analytical blanks were within  $1 \times 10^{-9}$ , and  $1 \times 10^{-10}$  cm<sup>3</sup> STP for  $^4\text{He}$ , and  $^{36}\text{Ar}$ , respectively, for both fusion and crushing experiments.

## 4. Measurements

[8] The first three columns of Table 1 show the measured initial noble gas abundances: the  $^4\text{He}$ -concentrations, the  $^3\text{He}/^4\text{He}$ -ratios as well as the ratios of  $^4\text{He}$  to radiogenic  $^{40}\text{Ar}^*$  of the samples from three different depths (fraction 1).

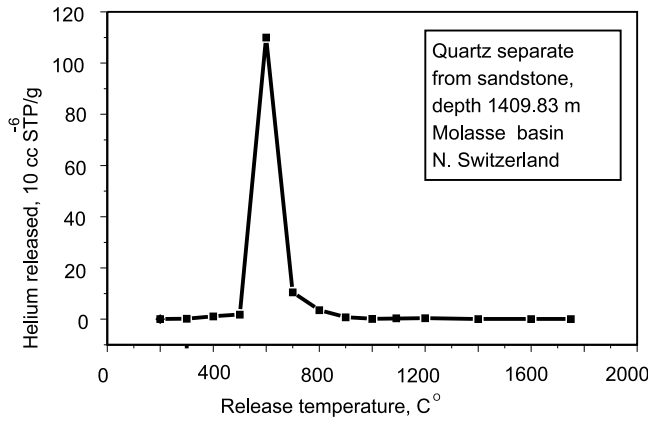
[9] To understand the degree of initial (natural) saturation of quartz with helium, the He-accessible volume within the minerals should be quantified. This volume consists of defects in the crystal lattice and gas/fluid inclusions formed during growth and evolution of the crystals. To perform the relevant impregnation/extraction experiments the acceptable temperatures should be constraint. First of all these temperatures should be high enough to allow a reasonable duration of the diffusion experiments, but not too high, so that the accessible He-sites within the crystal are preserved. The helium release pattern under step-wise heating of the mineral gives  $\leq 350^\circ\text{C}$  as a reasonable upper limit: less than 1% of the total amount of He was released below this temperature (Figure 1).

[10] A helium pressure of  $p = 32$  atm at a lower temperature of  $T = 290^\circ\text{C}$  was selected for the saturation experiments. Two related samples (fractions 2 and 3, separated from the same piece of sandstone) were exposed under these pT conditions during 504 hours and 1412 hours, respectively. Then helium was extracted from the saturated samples and its quantity was measured. Similar post-saturation helium concentrations resulted (Table 1), indicating that indeed the samples were most likely saturated with helium.

[11] The measured  $^4\text{He}$ -content in the saturated samples (table) gives the He-accessible volume  $V_2$  of quartz by simply applying the gas law

$$V_2 = V_1 \cdot (p_1/p_2) \cdot (T_2/T_1) = V_1/15.5 \quad (1)$$

where  $V_1$  is the measured volume (cc STP  $^4\text{He}/\text{cm}^3$  of quartz) at the standard pressure ( $p_1 = 1$  atm) and the



**Figure 1.** Helium release pattern under step-wise heating of quartz separate (45 min for each step). Notice negligible loss of helium under heating below 350°C. Most defects are preserved under this temperature, which was chosen as an upper limit for the He-saturation — extraction experiments.

standard temperature ( $T_1 = 273$  K), and  $p_2 = 32$  atm and  $T_2 = 290^\circ\text{C} = 563$  K are the relevant parameters of the impregnation experiments. The calculated He-accessible volumes for the 10 measurements are in a range of 0.018% to 0.13% (Table 1).

## 5. Mineral-Fluid Equilibrium

[12] The helium concentration in the pore fluid can only be unambiguously related to the concentration in quartz if a fluid-mineral equilibrium exists. To examine whether the equilibrium has been achieved or not, the effective diffusion coefficient was estimated for the sample from a depth of 1250.34 m using isothermal helium release (Figure 2).

[13] Assuming that a cube of size  $(0.33 \text{ mm})^3$  is representative for the ensemble of the selected grains, the release pattern at 350°C (Figure 2) gives an estimated apparent diffusion coefficient of about  $1 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ , similar to those obtained for quartz in other experiments [Trull *et al.*, 1991]. To extrapolate from the temperature of 350°C of our  $^4\text{He}$ -recovery experiment (Figure 2) to the formation temperature (in Kelvin) of the groundwater sample at 1415 m in the Weiach borehole (70°C) we use an Arrhenius equation derived from the data of Trull *et al.*:

$$\log D = \log D_0 - 5430/T = -0.28 - 5430/T \quad (2)$$

which yields a value of  $D \sim 10^{-16} \text{ cm}^2/\text{s}$ .

[14] A characteristic time to reach an equilibrium by diffusion is estimated from the expression  $x = (D \cdot t)^{1/2}$  where  $x$  represents an average diffusion length of 0.17 mm (the half-size of our representative quartz cube). At  $T = 290^\circ\text{C}$  the calculated equilibration time is 800 hours; at  $T = 70^\circ\text{C}$  it is 90 000 years.

[15] Although these times are to be taken as order of magnitude estimates only, they illustrate that (i) the exposure time for determining the He-accessible volumes in our experiments was of the right magnitude and that (ii) in the sandstone/shale interlayering in the Permo-Carboniferous Trough where the helium residence time is estimated to be several million years (B. Lehmann, manuscript in prepara-

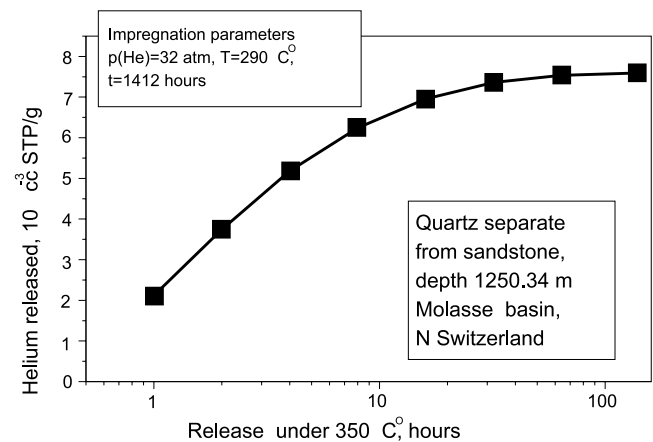
tion, 2003) the transfer of helium from pore- or groundwater into quartz and vice versa is fast enough to reach equilibrium.

## 6. Discussion

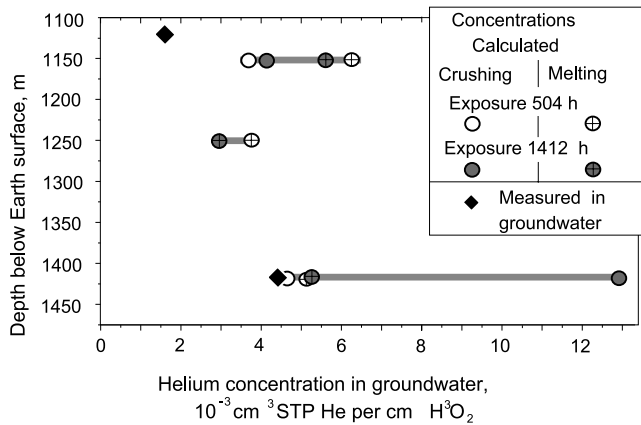
[16] One of the three sandstone samples (1409.83 m) is very close to the depth of 1408 m from which a groundwater sample was taken during the deep drilling project. This sample contains a rather high  $^4\text{He}$ -concentration of  $4.5 \cdot 10^{-3} \text{ cc STP/cm}^3$  of water [Pearson *et al.*, 1991] which corresponds to a partial helium pressure in an associated gas phase of 0.47 atm, for a solubility of helium in water of  $S = 9.5 \cdot 10^{-3} \text{ cc STP/(cm}^3 \text{ of water} \cdot \text{atm)}$  at  $T = 70^\circ\text{C}$ . This pressure is surprisingly close to the pressure one can derive for the helium gas inside the quartz (fractions 2 and 3 of sample 1409.83 m; see Table). For example, the concentration of  $0.11 \cdot 10^{-3} \text{ cc STP/cm}^3$ , obtained by melting of the powder, yields  $p = 0.55$  atm in the He-accessible volume of  $0.25 \cdot 10^{-3} \text{ cm}^3$  at  $T = 70^\circ\text{C}$ . Similar values are obtained for 9 out of 10 measurements.

[17] The conclusion is that helium is most likely in a gas phase in the small volume of the defects (including fluid inclusions) in quartz and is in a simple solubility equilibrium with the surrounding ground- or porewater. The measured  $^4\text{He}/^{40}\text{Ar}$ -ratios of the extracted gas (Table) are very high compared to e.g., an average crustal production ratio of about 5 and it therefore appears, that these sites inside the quartz crystals are not accessible to Ar atoms (and not to water molecules either).

[18] Helium isotope abundances in rocks, minerals, and groundwaters of the Permo-Carboniferous Trough under the sediments of the Molasse basin in Northern Switzerland allow the helium behaviour to be reconstructed: both  $^3\text{He}$  and  $^4\text{He}$  are mainly produced in shales, having high concentrations of parent elements (U, Th, Li). Then these isotopes are released into pore-fluids and into aquifers; from pore fluids or aquifers some helium atoms penetrate into rock-forming minerals, such as quartz. Provided that a



**Figure 2.** Cumulative helium release from the saturated sample under constant temperature. The saturation conditions (pressure, temperature and time) are shown. Assuming diffusion is the principal mechanism of helium loss from a cubic sample having size  $(0.33 \text{ mm})^3$ , an apparent diffusion coefficients of about  $10^{-9} \text{ cm}^2 \text{ s}^{-1}$  is estimated from this figure.



**Figure 3.** Helium concentrations in porewaters calculated based on a solubility equilibrium between water and quartz grains (equation 3). Two measured concentrations in groundwater shown for comparison.

solubility equilibrium between helium concentrations in the minerals and the fluids has been established (as demonstrated in the present study), the observed helium concentrations in minerals  $c_{\text{ini}}$  enable us to recover the concentrations in pore fluids  $c_w$

$$c_w = S \cdot (c_{\text{ini}}/V_2) \cdot (343/273) \quad (3)$$

where  $V_2$  is the He-accessible internal volume (see equation 1) and 343 K and 273 K are the formation and standard temperatures, respectively.

[19] Indeed, concentrations  $c_w$  calculated from Table 1 (by equation 3) are very close to the two available measured concentrations in groundwater in this depth range (Figure 3). We would like to point out that this approach in particular can be applied to impermeable rocks where in-situ pore-water samples are generally not available. Note that in these preliminary experiments the initial  $^4\text{He}$ -content was measured on a separated fraction 1 of quartz crystals before it was realized that the internal volumes differ. In particular, one value of  $c_w$  in Figure 3 (1409.83 m, crushing after exposure for 1412 h) is well outside the average for the other samples, most likely because one (or a few) larger bubbles were present in this fraction. For future experiments

it is therefore important to determine the He-content and the He-accessible volume using the very same sample and preliminary experiments showed that this is possible.

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